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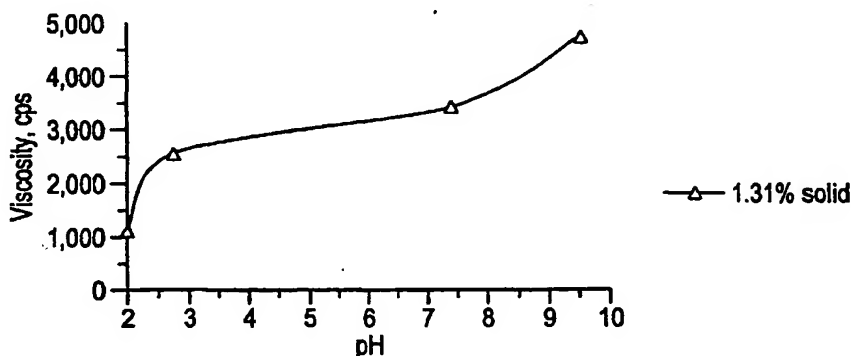
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(54) Title: CROSSLINKED CATIONIC MICROGELS, PROCESS FOR MAKING SAME AND HAIR CARE COMPOSITIONS THEREWITH



(57) Abstract: What is described herein is a fine particulate, crosslinked cationic microgel which is capable of adsorbing up to 200 times its dry gel weight of water, and which has a viscosity of 5870 cps in water at a pH of 2.8 adjusted with a divalent or trivalent acid, at a copolymer concentration of about 1 %. The microgel includes, by weight, about 5-95 %, preferably 50 % of a water soluble monomer which is vinyl pyrrolidone (VP), and about 5-95 %, preferably 50 %, of a water soluble cationic monomer which is 3-dimethylaminopropyl-(meth)acrylamide (DMAPMA) and a low crosslinker content, e.g. about 0.2 %. The copolymers are made by a solution polymerization process from a mixture of VP and DMAPMA, crosslinker, solvent and initiator. The invention also describes hair care composition which include, by weight, about 0.01-5 % of such microgel polymers, and water, at a low pH, which exhibit conditioning and styling of the microgel copolymer and water. In shampoo formulations, optionally an anionic surfactant is included.

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CROSSLINKED CATIONIC MICROGELS,  
PROCESS FOR MAKING SAME AND  
HAIR CARE COMPOSITIONS THEREWITH

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to hydrogels, and, more particularly, to crosslinked cationic microgel dispersions in aqueous solutions, which can form thick deposits on hair or skin surfaces to modify the properties of such surfaces.

2. Description of the Prior Art

Polymeric crosslinked polyacrylic acid thickeners have been used to modify the physical form, function and aesthetics of personal care formulations. However, such anionic hydrogels do not maintain their thickener action at a low pH and they are not compatible with a cationic formulation.

Similarly, Aizawa, T. et al, in U.S. Pat 5,338,815, described the preparation of fine particulate crosslinked N-vinylamide homo- and co-polymers, particularly poly-N-vinylformamide and poly-N-vinylacetamide, which had thickening properties in neutral water, (pH 6-8), for application in lotions and creams, and in industrial products.

Other references of interest are U.S. Pats. 5,663,258 and 5,684,105; Y. Zhong and P. Wolf, Hydrogel Prepared from Crosslinked Vinyl Pyrrolidone and Vinyl Acetate Copolymer, *Polymer Reprints* **1997**, 38 (2), p. 578; and Y.

Zhong and P. Wolf, Swelling Properties of Crosslinked Vinylpyrrolidone Homopolymers and Vinylpyrrolidone/Vinyl Acetate Copolymers, *Polymer Reprints* 1998,39 (2), p. 461.

Accordingly, it is desired to provide a crosslinked cationic microgel copolymer capable of adsorbing large amounts of water per weight of polymer and to provide an effective viscosity even at low pH.

Another object of this invention is to provide a hair care composition having thickening, conditioning and styling properties even at low pH.

These and other objects and features of the invention will be made apparent from the following description thereof.

#### IN THE DRAWINGS

FIG. 1 is a plot of viscosity in cps vs. pH adjusted with  $H_2SO_4$  for XL-PVP/DMAPMA a cationic copolymer microgel composition of invention in water at a solids content of 1.31%, having a monomer unit ratio of 80/20 by weight and crosslinker in an amount of 0.45% of monomers.

FIG. 2 is a similar plot of viscosity vs. pH adjusted with HCl for a XL-PVP/DMAPMA cationic copolymer microgel compositions of invention in water at a solids contents of 1.13%, 0.57% and 0.40%, respectively, having a monomer unit ratio of 50/50 by weight and crosslinker is 0.20% of monomers.

FIG. 3 is a plot of water adsorption vs. time for a dry XL-PVP/DMAPMA cationic copolymer in neutral pH, in comparison with the non-ionic XL-PVP homopolymer, the copolymer having a monomer unit ratio of 50/50 by weight and crosslinker is 0.20% of monomers.

FIG. 4 (a) is a plot of combing force differences (G) vs. distance (mm) along the hair tresses on which has been applied a control hair care shampoo formulation without additive, before and after treatment) after shampooing showing an increase in combing forces.

FIG. 4 (b) is a similar plot for treatment with formulations of the cationic microgel of the invention showing a decrease in combing forces.

FIG. 5 is an actual photograph of (a) untreated virgin hair, (b) hair treated with the control hair care shampoo formulation (no additive) and (c) hair treated with a formulation containing the cationic microgel of the invention.

### SUMMARY OF THE INVENTION

What is described herein is a fine particulate, crosslinked cationic microgel which is capable of adsorbing up to 200 times its dry gel weight of water, and which has a viscosity of 5780 cps in water at a pH of 2.8 adjusted with a divalent or trivalent acid, at a copolymer concentration of about 1%. The microgel includes, by weight, about 5-95%, preferably 50% of a water soluble monomer which is vinyl pyrrolidone (VP), and about 5-95%, preferably 50%, of a water soluble cationic monomer which is 3-dimethylaminopropyl-(meth)acrylamide (DMAPMA) and a low crosslinker content, e.g. about 0.2%. The copolymers are made by a solution polymerization process from a mixture of VP and DMAPMA, crosslinker, solvent and initiator. The invention also describes hair care composition which include, by weight, about 0.01-5% of such microgel polymers, and water, at a low pH, which exhibit conditioning and styling of the microgel copolymer and water. In shampoo formulations, optionally an anionic surfactant is included.

### DETAILED DESCRIPTION OF THE INVENTION

The hair care compositions of the invention contain a cationic copolymer which is XL-PVP/DMAPMA, i.e. a crosslinked vinyl pyrrolidone and 3-dimethylaminopropyl methacrylamide copolymer, as a conditioning agent for hair. This crosslinked copolymer forms microgel dispersions in aqueous

solutions which provide relatively thick and lubricious layers on the surface of hair. Unlike linear, uncrosslinked cationic polymers, which lay flat on the hair surface, the swollen microgel particles of the crosslinked polymer of the invention forms thick deposits which significantly modify the surface properties of hair.

This copolymer also can be used effectively in anionic surfactant-based shampoo compositions which ordinarily do not provide a favorable medium for deposition of linear cationic polymers or surfactants. The XL-PVP/DMAPMA copolymer of the invention, in contrast, when used for example as a 1% solution, provides excellent conditioning as evidenced by wet and dry combing evaluations. Specifically, shampoo compositions containing 0.5% copolymer showed a significantly better conditioning performance than linear cationic polymers such as Styleze® CC-10 or Polymer JR® 400. In addition, the deposited copolymer layer from the microgel of the invention also provides links between fibers after drying, thus resulting in a styling or fixative effect, which remains intact even after repeated rinsing with water after shampooing.

Such conditioning and styling properties can also be obtained with cationic microgels of the following copolymers:  
XL-Acrylamide/DMAPMA, XL-poly(vinyl caprolactam) (PVCL)/DMAPMA and XL-Acrylamide/dimethylaminoethyl methacrylate (DMAEMA).

The XL-PVP/DMAPMA copolymer solutions of the invention have a low viscosity at high pH, where the amines are essentially uncharged. However, upon addition of a suitable acid, preferably a di- or tri- hydric acid, the pH drops and positive charges are generated on the polymer side chains as the amine monomer is protonated. The repulsion forces developed between these positive charges causes the polymer to swell, enabling the cationic hydrogel to be used effectively as a thickener at a low pH.

The unique characteristics of XL-PVP/DMAPMA thus include:

- (1) High viscosity upon addition of acid.

Representative results: (vis. = Brookfield viscosity, cps)

XL-PVP/DMAPMA in water with addition of concentrated H<sub>2</sub>SO<sub>4</sub>:

% solid = 0.86, pH 9.74, vis. = 650; pH 2.48, vis. = 5,870 (an increase of 9 times).

- (2) The viscosity can be controlled at low pH with addition of a suitable acid:

When acid was added to the copolymer solution, preferably a di- or trihydric acid, such as sulfuric acid or phosphoric acid, its viscosity increased sharply, however, with too much acid, its counter-ion shielding effect on polyelectrolytes caused the viscosity to drop. With H<sub>2</sub>SO<sub>4</sub>, the viscosity remained high at a pH even as low as 2.48.

- (3) Extremely high capacity for adsorbed water:

0.1 g of dry XL-PVP/DMAPMA adsorbs 1.7 grams of deionized water (170 times its weight).

The composition of the XL-PVP/DMAPMA copolymer, by weight, is as follows:

	<u>Suitable</u>	<u>Preferred</u>	<u>Optimum</u>
VP	5-95	20-80	40-60
DMAPMA	5-95	20-80	40-60

Suitable crosslinkers include pentaerythritol triallyl ether (PTE) and methylene-bis-acrylamide (BIS).

Suitable initiators for the polymerization reaction include tertiary butyl peroxy pivalate (Lupersol® 11) and tertiary amyl peroxy pivalate (Lupersol® 554).

During the polymerization reaction, the total monomer level suitably is maintained at about 5-80%, preferably about 10-50%, and optimally about 15-30%.

During the polymerization reaction, the crosslinker level suitably is maintained at about 0.01-5%, preferably about 0.1-2%, and optimally about 0.2-1%, based on the weight of total monomer.

The invention will now be described in more detail with reference to the following examples.

### **EXAMPLES**

Monomers: VP: (International Specialty Products). DMAPMA: (Rohm America). Crosslinkers: Pentaerythritol triallyl ether (PTE),  $\text{HOCH}_2\text{-C}(-\text{CH}_2\text{-O-CH}_2\text{-CH=CH}_2)_3$  and methylene-bis-acrylamide (BIS), (Aldrich). Initiators: tertiary butyl peroxy pivalate (Lupersol® 11) and tertiary amyl peroxy pivalate (Lupersol® 554), (Lucidol). Solvent: Deionized water. Non-solvent: Heptane, (Aldrich).

#### **Solution Polymerization of Non-Crosslinked Copolymer.**

Monomers, initiators and solvent were added to a Buchi reactor through syringe pumps. The product was an aqueous solution of 50% copolymer.

#### **Precipitation Polymerization of Crosslinked Copolymer**

A non-solvent was added to a Buchi reactor, and, then monomers, crosslinker and initiators in heptane were added continuously. After vacuum drying, the product was obtained in powder form.

### **Solution Polymerization of Crosslinked Copolymer**

Monomers, crosslinker, initiator and solvent were added into a beaker, which was put into a vacuum oven and heated until the reaction was completed. A thin polymer layer formed at the bottom of the beaker. A large amount of distilled water was added to swell the polymer. A Ross homogenizer was used to break up the hydrogel.

### **Brookfield Viscosity Measurements**

The viscosity of aqueous copolymer solutions were measured with a Brookfield Digital Viscometer.

### **Swelling Volume Measurements**

A 1% (w/v) aqueous solution was stoppered and allowed to stand at room temperature for 2 days. The volume attained by the gel was recorded as the swelling volume with the units of ml/g.

### **Swelling Kinetics**

At room temperature, after equilibrium with water, a hydrogel disc was weighed after removal of excess surface water by light blotting with a laboratory tissue. The gel was completely dried in a microwave oven. Therefore the maximum amount of water absorbed was calculated. The dried gel was then placed into and taken out of water according to a schedule, and was weighed following the same method mentioned above. Therefore the swelling kinetics of Q (wet/dry) vs. time was determined.



**EXAMPLE 1****Swelling Property of Non-Crosslined Copolymer**

The Brookfield viscosity of aqueous solutions of non-XL PVP/DMAPMA, prepared by solution polymerization, was measured at various pHs, the results are given in Table 1 below.

**Table 1.** Brookfield Viscosity of Aqueous Solutions of Non-Crosslinked PVP/DMAPMA

Brookfield viscometer, Spindle model DV-II, Number 6.

Concentrated hydrochloric acid was added to adjust pH.

VP/DMAPMA (wt. ratio)	% Solids	pH	Brookfield Viscosity (cps)
80/20	4.3	7.19	3,300
		1.94	3,300
39/61	2.0	10.55	500
		8.49	700
		0.2	700

At the monomer ratios (DMAPMA, up to 61 wt. %, 50 mole %), even at very high polymer concentrations (up to 4.3%), the Brookfield viscosity of the aqueous solutions were very low, and no increase in viscosity was observed upon addition of acid over a very wide pH range. Accordingly, non-crosslinked PVP/DMAPMA does not possess any hydrogel property.

**EXAMPLE 2****Swelling Property of Crosslinked Copolymer****A. Prepared by Precipitation Polymerization**

The swelling volume of an aqueous solution of XL-PVP/DMAPMA, prepared by precipitation polymerization, was measured; the results are given below in Table 2.

**Table 2.** Swelling Volume of an Aqueous Solution of Crosslinked-PVP/DMAPMA Prepared by Precipitation Polymerization

VP/DMAPMA Ratio = 80/20 (wt), 86/14 (mole)

Crosslinker = 0.45% of monomer (by wt)

pH buffer reagent (Aldrich) was added to adjust pH.

% Solids	pH	Swell Volume (ml/g)
1%	2.0	30
	7.0	20

The crosslinked copolymer was swollen in water, and, when the pH was decreased from 7.0 to 2.0, the swelling volume increased from 20 to 30 ml/g. This increase, however, is not significant, compared with the swelling volume for a crosslinked copolymer prepared by solution polymerization.

### **B. Prepared by Solution Polymerization**

The Brookfield viscosity of an aqueous solution of XL-PVP/DMAPMA, prepared by solution polymerization, with different monomer and crosslinker ratios, was measured as a function of pH. The results are given in Figures 1\* and 2\*\*.

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\* Figure 1. Brookfield viscosity of crosslinked PVP/DMAPMA (made from solution polymerization) in water under various pH. VP/DMAPMA = 80/20 by wt, XL = 0.45% of monomers (by wt). Brookfield Viscometer, model DV-II spindle, Number 4. pH was adjusted by addition of concentrated sulfuric acid.

\*\* Figure 2. Brookfield viscosity of crosslinked PVP/DMAPMA (made from solution polymerization) in water under various pH. VP/DMAPMA = 50/50 by wt, XL = 0.20% of monomers (by wt). Brookfield Viscometer, Model T spindle, Number 4. pH was adjusted by addition of concentrated hydrochloric acid.

At a monomer wt. ratio for VP/DMAPMA of 80/20 and crosslinker at 0.45 wt. %, the copolymer hydrogel had a much higher viscosity than the viscosity of the non-crosslinked copolymer given in Table 1 (See Fig. 1). However, there is no discernible trend of an increase in viscosity upon addition of H<sub>2</sub>SO<sub>4</sub> acid. In fact, at a lower pH, the viscosity decreased as well.

In contrast, when the proportion of amine monomer was increased to 50% and the amount of crosslinker was decreased to 0.20%, the unique character of the cationic hydrogel was observed, as shown in Figure 2. At a high pH, the polymer solution has a very low viscosity. However, upon addition of HCl acid, the pH drops and viscosity increases sharply. The resultant hydrogel had an extremely high viscosity even at a very low copolymer concentration.

**EXAMPLE 3**  
**Effect of a Given Acid on Viscosity**  
**Of XL-PVP/DMAPMA Solutions**

As shown in Figure 2, with an excess of added HCl acid, the viscosity of the acidic solution dropped, which is attributed to the counter-ion shielding effect on polyelectrolytes. However, the effect of acid on viscosity is sensitive to the specific acid used, as shown in Table 3 below.

**Table 3.** Brookfield Viscosity of Aqueous Solutions of Crosslinked PVP/DMAPMA Prepared by Precipitation Polymerization

Brookfield viscometer, Spindle model DV-II, Number 3.  
Concentrated sulfuric acid was added to adjust pH.

VP/DMAPMA (wt ratio)	% Solids	pH	Brookfield Viscosity (cps)
50/50	0.86	9.74	650
		2.48	5,870

With sulfuric acid, the viscosity of the acidic copolymer solution was very high at pH 2.48 (9 x the viscosity at pH 9.74); while with hydrochloric acid, as shown in Figure 2 viscosity dropped when pH was below 7, and became zero at a pH of 3.

**EXAMPLE 4****Swelling Kinetics of Crosslinked Copolymer****Prepared by Solution Polymerization**

The high water adsorption capacity of XL-PVP/DMAPMA (in comparison with XL-PVP) was demonstrated by the swelling isotherms given in Figure 3.

**Figure 3.** Swelling isotherms of XL-PVP/DMAPMA and XL-PVP in neutral water (pH 6.68). XL-PVP/DMAPMA was made from solution polymerization, VP/DMAPMA = 50/50 by wt, XL = 0.20% by wt. of monomers.

XL-PVP/DMAPMA absorbed water in an amount up to 200 times by wt of the dry gel, which is more than 10 times the capacity of non-ionized XL-PVP.

**EXAMPLE 5****Conditioning Shampoo Formulation****Part A**

- 15% Ammonium Lauryl Sulfate (Standapol A, Henkel Corporation)
- 15% Sodium Lauryl Sulfate (Rhodaon SB-8208/S, Rhône Poulenc)
- 8% Cocamidopropyl Betaine (Mirtaine CB, Rhône Poulenc)
- 2% Lauramide DEA (Monamid 716, Mona Industries)

**Part B**

- 1% Conditioning Additive
- 58.8% Deionized H<sub>2</sub>O

**Part C**

- 0.2% Diazolidinyl Urea/Iodopropynyl Butylcarbamate (Germall Plus, ISP)

### Instructions

Heat Part A to 60°C with moderately slow stirring for approximately ½ hour or until solution becomes transparent. At the same time, heat Part B to 55°C while stirring until homogeneous solution is obtained. Add Part B to Part A while continuously stirring. Remove temperature source. Once the resulting solution has reached 45°C, add Part C. Continue to stir (slowly) until the target solution has cooled to an ambient temperature.

Shampoo formulations without additive (Fig. 4 (a) and with additive 4 (b)), were applied to a limited area on a tress by placing the fiber in a special frame with two windows. The shampoo treated hair only in the two windows are. The vent of the tress was untreated. The results indicate that (1) color sample treated with shampoo without constituting showed no consistency effect. On the color treated area displaced an increase in combing .

Fig. 5 shows the advantageous effect of binding hydrogel to the hair 5(c) compared to non-binding for untreated hair 5(a) and control treated hair 5(b)

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art. Accordingly, it is intended to be bound only by the following claims, in which:

**WHAT IS CLAIMED IS:**

1. A fine particulate, crosslinked copolymer cationic microgel which is capable of adsorbing many times its weight of water, consisting essentially of, by weight, about 5-95% of a water soluble monomer which is vinyl pyrrolidone (VP), and about 5-95% of a water soluble cationic monomer which is 3-dimethyl-aminopropyl(meth)acrylamide (DMAPMA).
2. A microgel according to claim 1 wherein (a) is 20-80% and (b) is 20-80%.
3. A microgel according to claim 1 wherein (a) is 40-60% and (b) is 40-60%.
4. A hair treatment composition comprising, by weight, about 0.01-5% of the microgel copolymer of claim 1, and water, at a low pH.
5. A composition according to claim 4 which includes about 0.1-2% of said microgel copolymer.
6. A hair care composition exhibiting conditioning, styling and cleansing properties, comprising the microgel copolymer of claim 1, water, and an anionic surfactant.

7. A hydrogel composition comprising 1.22% of the microgel of claim 1 and about 98.78% water.

8. A solution polymerization process of making the crosslinked cationic microgel of claim 1 comprising providing a mixture of VP and DMAPMA, crosslinker, solvent and initiator, and polymerizing the mixture in a vacuum oven at about 60°C for about 1½ hours, then at about 120°C for about 1.5 hours, washing the resultant polymer film in water to remove unreacted monomers, and homogenizing the swollen gel into a microgel.

9. A process according to claim 8 wherein the final concentration of solids in the microgel is about 1.13% at a pH of 8.32, and the Brookfield viscosity is 157,000 cps (T type spindle # E).

10. A process according to claim 8 wherein the crosslinked copolymer is about a 50/50 (w/w) of VP/DMAPMA and the crosslinker is present at about 0.2% by wt. of monomers.



1 / 4

FIG. 1

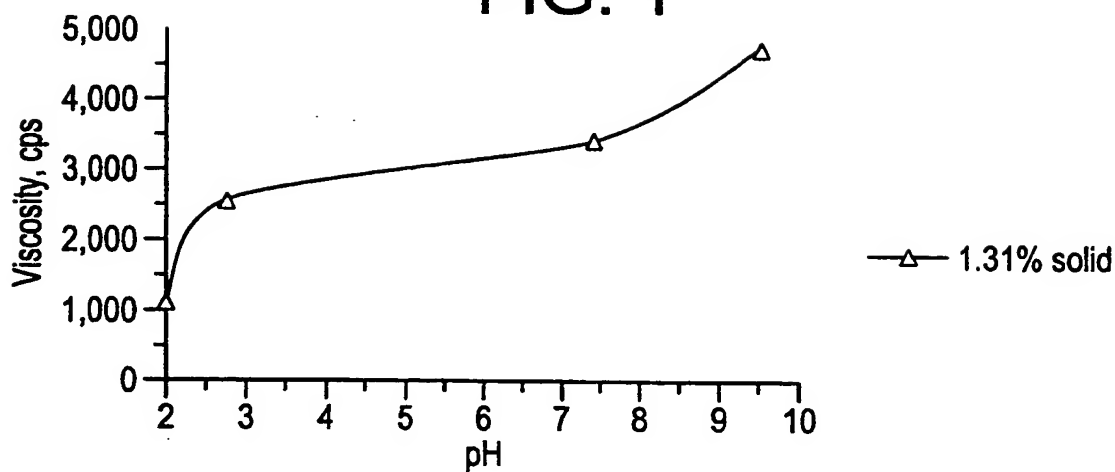


FIG. 2

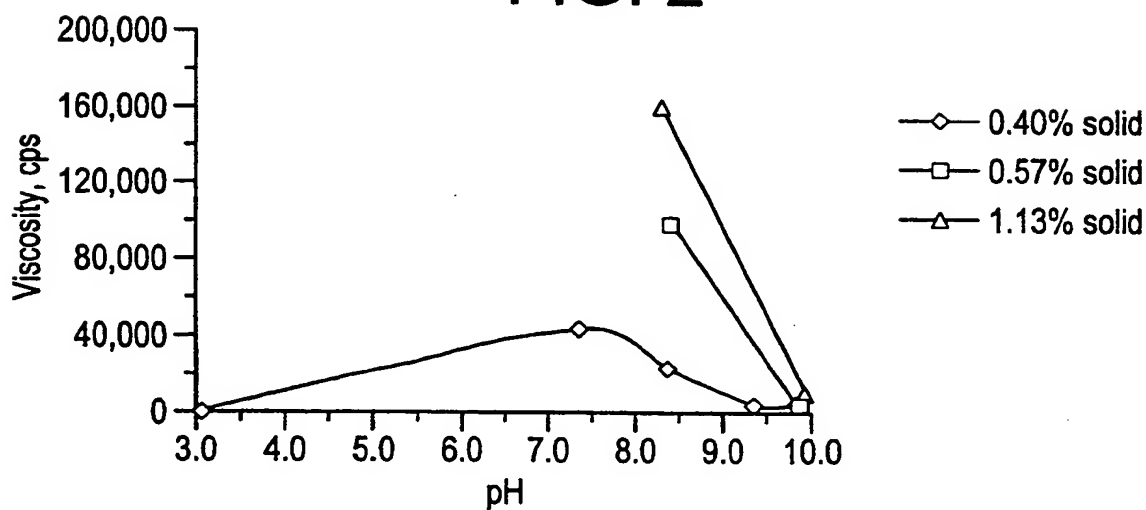


FIG. 3

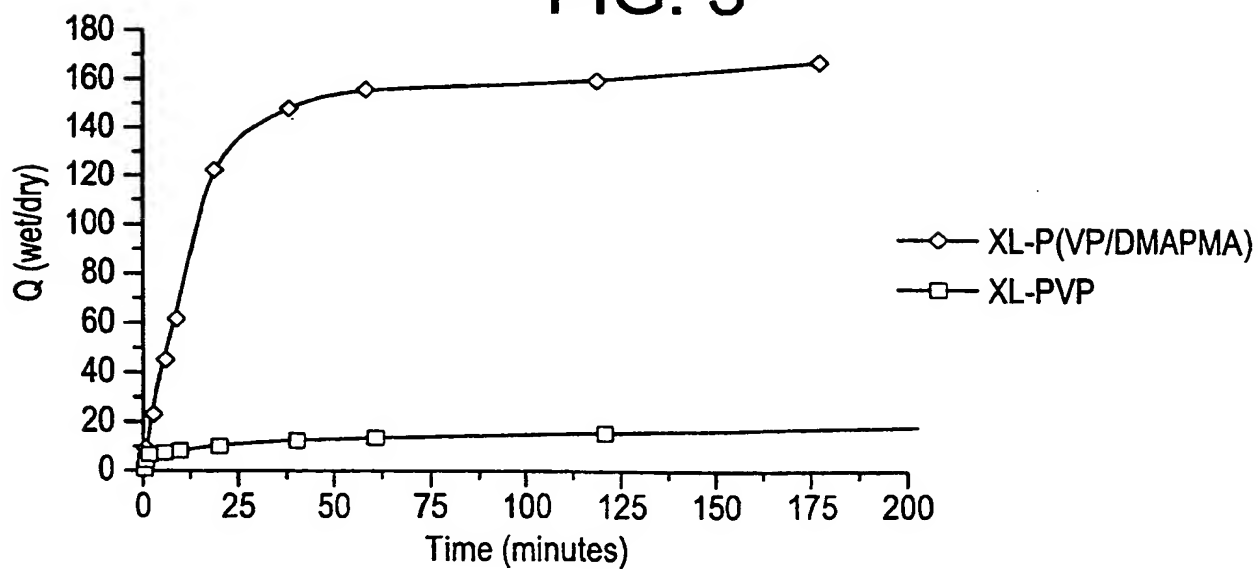


FIG. 4A

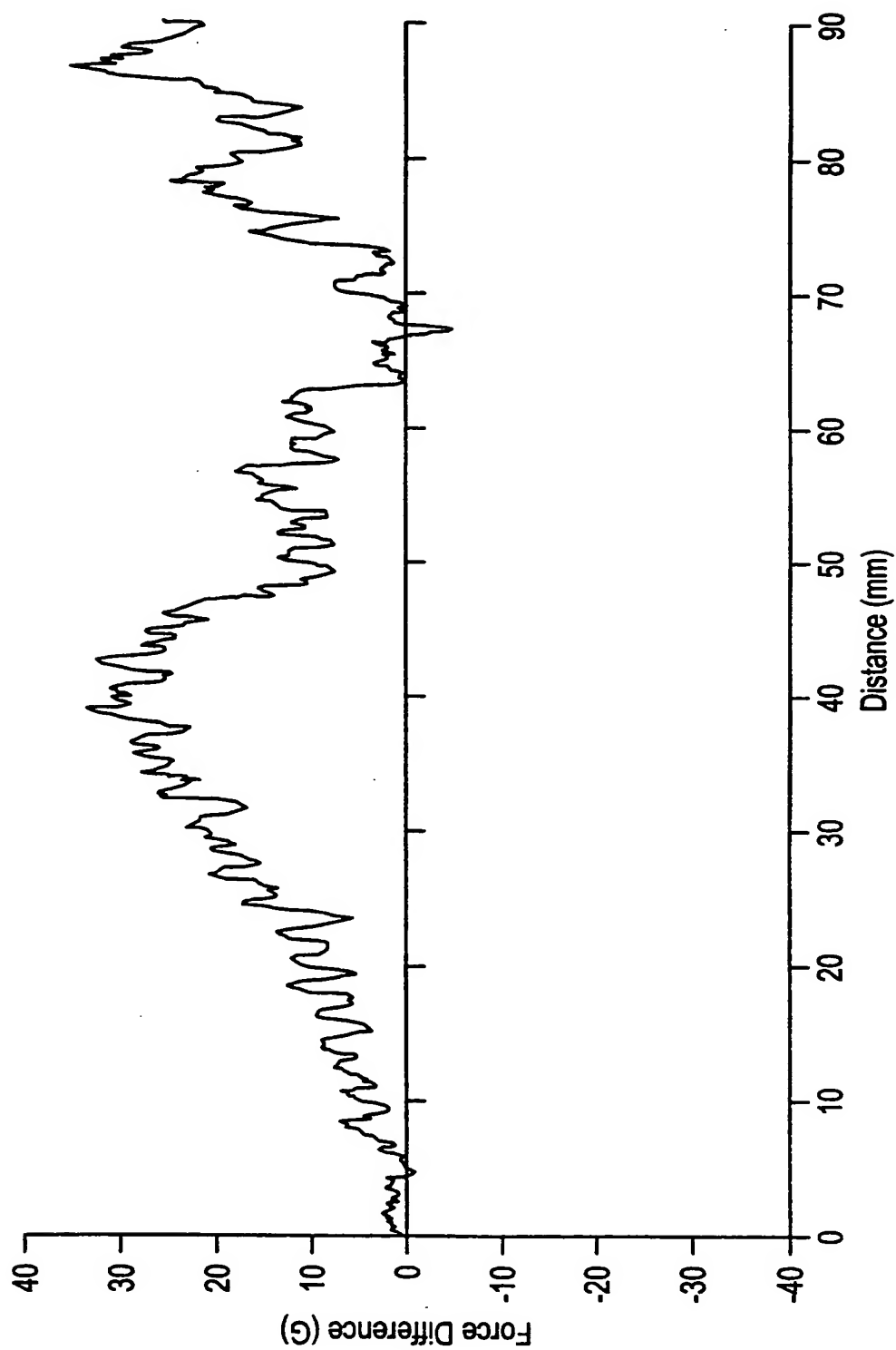


FIG. 4B

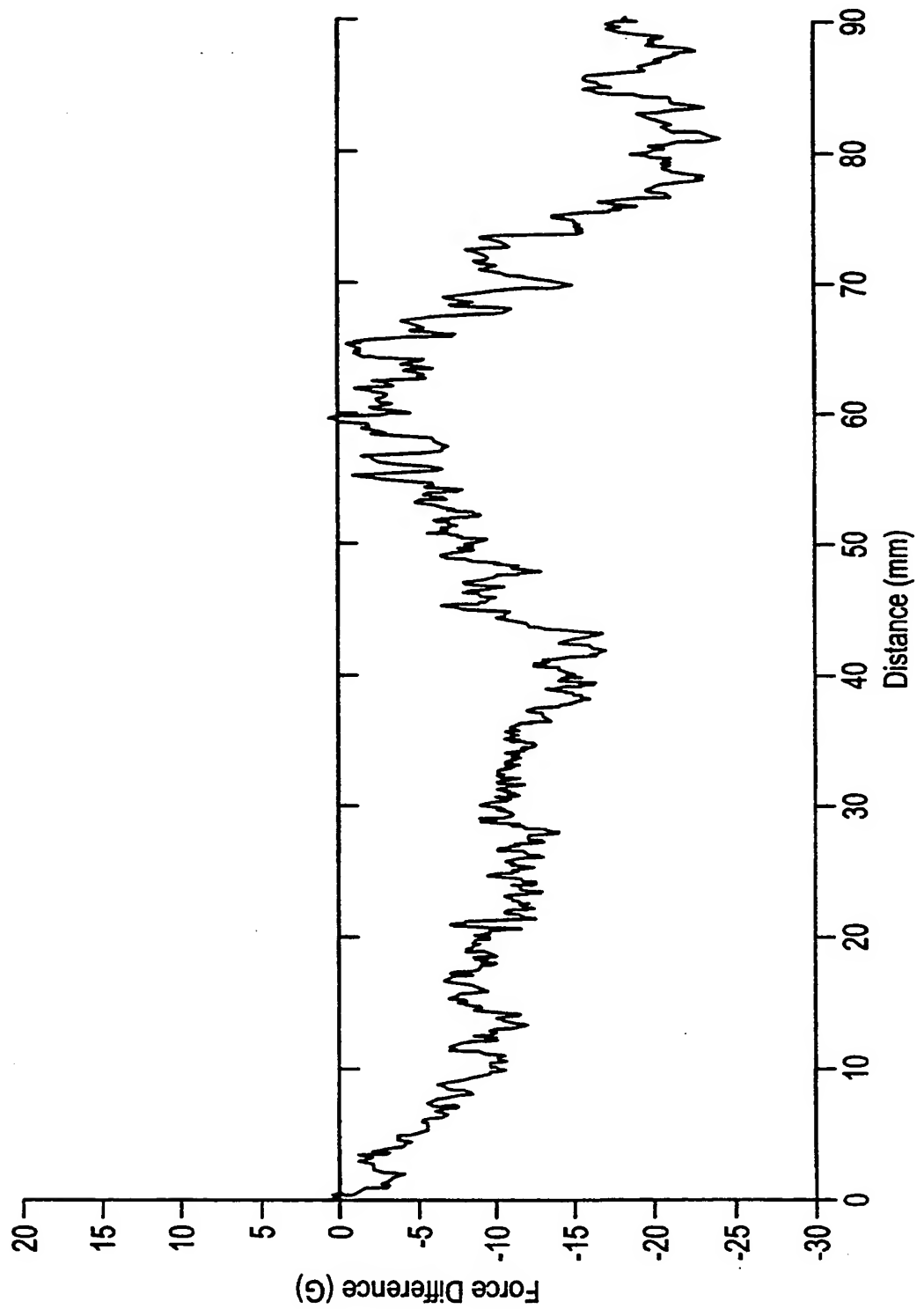
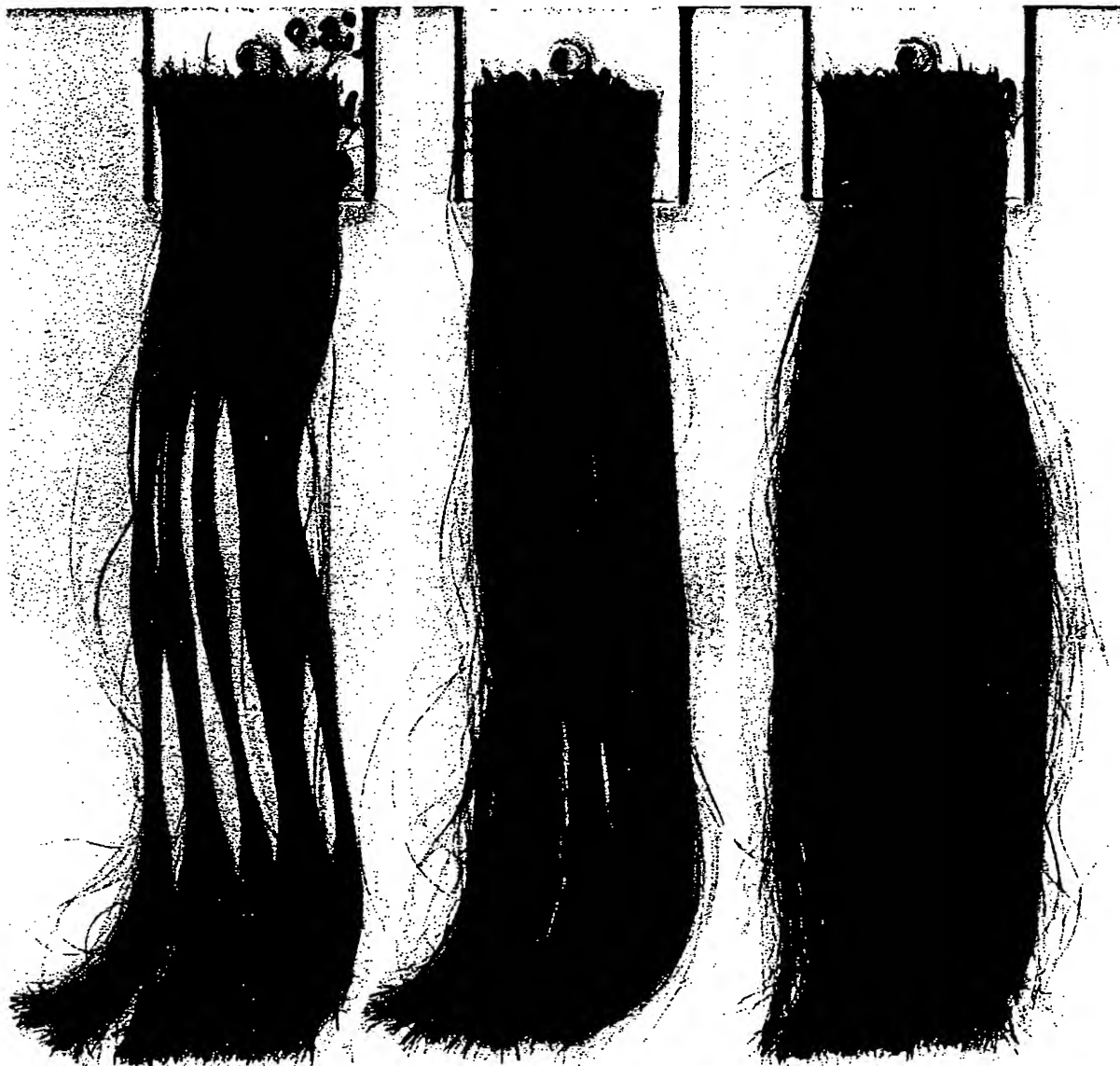


FIG. 5C

FIG. 5B

FIG. 5A



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/12858

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A61K 7/06, 7/08; C08F 226/10

US CL : 424/70.1, 70.11, 70.15, 70.16, 70.22; 526/264

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70.1, 70.11, 70.15, 70.16, 70.22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----	US 5,717,045 A (TSENG) 10 February 1998, see entire document.	1-3 & 7-10 ----
Y		4-6
X ----	US 5,321,110 A (SHIH) 14 June 1994, see entire document.	1-5 & 7-10 ----
Y		6
X,P	US 5,997,855 A (LIU) 07 December 1999, see entire document.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
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